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DUAL ADSORPTION ON NEGATIVELY CHARGED SURFACES IN NON-AQUEOUS MEDIA

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ABSTRACT

Titanium hydride powders with negatively charged surfaces cannot be dispersed by anionic polymers. Using low dielectric constant liquids further complicates dispersion by increasing surface charge while reducing the charge at the shear layer. It is possible to provide stabilization by employing two polymers that reverse and increase the magnitude of the surface charge. The same non-ionic polymer can then be used in the steric dispersion of both negatively and positively charged particles. This greatly improves process flexibility and allows the use of steric dispersants that under normal circumstances could not be used.

INTRODUCTION

There are many cases where it would be desirable to use a specific polymer dispersant to achieve slurry stabilization. Unfortunately, use can be prohibited by charge restraints. This investigation suggests a method of dispersing negatively charged titanium hydride (TiH_2) powder with an anionic surfactant and a particle bonded coupling agent.

Proper slurry dispersion is a necessary criterion for many processing applications. The powder constituent of the slurry is first mixed with a liquid medium. Brownian motion leads to frequent collisions between particles. These particles will agglomerate if there exists a net attractive force between them. To prevent agglomeration, polymers soluble in the slurry solvent are used to coat particle surfaces. Interaction between adsorbed polymer layers prevents agglomeration and can ultimately result in high solids loading while retaining low viscosity.

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Low molecular weight poly-methyl methacrylate (PMMA) is able to sterically stabilize powders in non-aqueous systems and provide additional processing benefits. PMMA is highly soluble in organic liquids, favors film formation on solvent evaporation, and volatizes completely on firing. PMMA has polar functional groups when dissolved in polar liquids. When pH is less than 4, PMMA is uncharged. As pH increases with the addition of a base, the PMMA molecule becomes negatively charged through the carboxyl dissociation process[1].

Anionic surfactants typically consist of a relatively long, lyophobic, nonpolar hydrocarbon chain terminated by a negatively charged lyophilic group at the surface-active head of the molecule[2]. In systems such as Al_2O_3 and TiO_2, PMMA can be used to successfully stabilize the slurry because the oxides carry a positive charge upon immersion. Positive sites on particle surfaces serve as points of attachment for the negatively charged portion of the polymer molecule. When polymer coated particles approach, overlap between adsorbed polymer layers provides an osmotic repulsive force due to the increase in the free energy of mixing between polymer and solvent[3]. This kind of dispersion is termed "steric stabilization".

TiH_2 is difficult to disperse in acetone because of the large, negative charges developed at the particle surface. Large potentials arise from the dielectric constant of acetone, which is approximately 4 times lower than that of water[4]. Negative charges likely arise from non-stoichiometry associated with hydrogen vacancies at the surface[5]. Additionally, surface potentials reported for the chemisorption of H_2 on transition metals are all negative[6]. Confirmation of negative surface charges in acetone were demonstrated by the measurement of ζ-potentials in the -100 mV range. The failure of charge alone to disperse TiH_2 indicates the importance of steric stabilization in these systems.

EXPERIMENTAL PROCEDURE

Raw TiH_2 as-received from Reading Alloys, Inc. contained particles as large as 1 mm and as such were undesirable for powder processing applications. The particles were ball milled in inert containers backfilled in a glove box with ultra high purity Ar. This inert atmosphere reduces the reaction of TiH_2 with contaminant gases such as oxygen and nitrogen during the milling process. Milling of each 250 g powder batch was achieved through action of approximately 100 stainless steel ball bearings, $^3/_8$ inch in diameter, for 64 hours.

Several materials were evaluated as dispersants and binders for the preparation of TiH_2 slurries. Elvacite 2008 grade PMMA was obtained from ICI Americas, Inc. (ICI). When green bodies containing PMMA are fired in an inert atmosphere, PMMA breaks down into the methyl methacrylate monomer and vaporizes between 200 and 430 °C, leaving no residue[7].

Dow Corning Z 6020 silane (ethylene diaminepropyl trimethoxysilane) was used to precoat the surface of the TiH_2 powder prior to the addition of acetone. To provide effective dispersion, 5 wt.% silane was first dissolved in A.C.S. reagent grade methanol (CH_3OH). The solution was mixed with the powder at a low shear rate. The methanol was allowed to evaporate completely and the resulting powder cake gently broken up using a mortar and pestle. TiH_2 precursor powder prepared in this manner will be considered "silane treated".

A.C.S. reagent grade acetone (CH_3COCH_3) was used as the polymer solvent and as the carrier vehicle for the TiH_2 powder. Acetone is suitable for the process because it is inert with respect to the TiH_2 powder, polymer additives, and containers, and allows rapid evaporation due to high volatility.

To conduct particle size measurements, aqueous suspensions were prepared containing 1.0 vol.% powder. Agglomeration was prevented by adding several drops of Darvan 851 from R. T. Vanderbilt and milling briefly. A Leeds and Northrup particle size analyzer, model 7997-20 was used in the measurements. After milling for 64 hours, particle size analysis confirmed that the TiH_2 powder ranged from 1 to 10 μm diameter with an average particle size of 6 μm.

To construct adsorption isotherms of PMMA on TiH_2 powder, dispersions were prepared with solid loadings of 20 vol.%. Lower concentrations than typically processed were used so that adequate amounts of acetone and polymer would be available for adsorption, the slurry would flow easily during mixing at all polymer concentrations, and enough supernatant would be available for analysis after centrifuging. The concentration of the polymer was determined by direct weighing following solvent evaporation. Weighed amounts of powder were mixed with polymer/acetone solutions. The mixture was shaken for 30 minutes at constant temperature to achieve adsorption equilibrium. The powder was then separated by centrifugation for 30 minutes. A known amount of clear supernatant was removed to determine equilibrium polymer concentration. The quantity of polymer adsorbed was then calculated from the change in concentration from the original polymer solution.

To construct adsorption isotherms of silane on TiH_2 powder, dispersions were prepared with solid loadings of 30 vol.%. Adsorption of silane onto TiH_2 powder was evaluated by (1) silane treating the powder and mixing with acetone and (2) mixing powder into a solution of acetone and silane. The mixture was shaken for 30 minutes at constant temperature to achieve adsorption equilibrium. The powder was then separated by centrifugation for 30 minutes. A small amount of the supernatant was withdrawn using a syringe. The index of refraction (n) of these solutions was measured using an Abbe refractometer, model 10450 manufactured by American Optical.

Standard solutions of acetone with known concentrations of silane were prepared to use in the determination of the amount of adsorbed silane. The indices of refraction of these solutions were measured together with the slurry samples to eliminate any effects of the refractometer and temperature fluctuations. The total amount of silane added to the slurry is a known quantity and the measured concentration in the supernatant can be found using the calibration curve. As a result, the amount of silane adsorbed onto the surface of the TiH_2 powder can be calculated.

A Brookfield LV type viscometer with associated cylindrical spindles was used for viscosity measurements.

RESULTS AND DISCUSSION

In this investigation, TiH_2 powder with a 1-10 μm particle size range and a 6 μm average particle size was dispersed in acetone using a variety of polymer combinations. PMMA disperses powders that are positively charged in acetone such as TiO_2 and Al_2O_3 but is ineffective on negatively charged TiH_2. Use of PMMA would be beneficial in the downstream processing of TiH_2.

The amount of polymer associated with monolayer coverage of TiH_2 is predicted using estimations of the surface area of adsorption. This value can be compared to measured adsorption isotherms[8]. The average area occupied by an adsorbing molecule, a, can be found using (1) where M is the molecular weight of the polymer, ρ is the density of the polymer, and N_A is Avogadro's number.

$$a = \left(\frac{M}{\rho \cdot N_A} \right)^{\frac{2}{3}} \tag{1}$$

The weight of polymer present in a monolayer can then be found by solving for W in (2) with knowledge of a and S, the surface area of the TiH_2 powder.

$$W = \frac{M \cdot S}{N_A \cdot a} \tag{2}$$

For ball milled TiH_2 powder having an average particle size of 6 μm, the specific surface area was found from B.E.T. analysis to be 1.6 m^2/g. A summary of the molecular weight, density, and predicted adsorption behavior of PMMA and silane can be found in Table I.

The experimental adsorption of PMMA onto TiH_2 particles in acetone can be found in Figure 1. The isotherm shows an affinity for PMMA at low equilibrium

Table I Summary of polymer characteristics and predicted adsorption behavior.

Polymer	M (g/mol)	ρ (g/cm^3)	a (m^2)	W (mg/g TiH$_2$)
PMMA	25 000	1.18	1.074×10^{-17}	6.183
Silane	180	1.03	4.383×10^{-19}	1.091

concentrations and a plateau representing monolayer coverage. Zeta potential measurements show that PMMA does not provide sufficient charge to disperse slurries electrostatically. TiH$_2$ is poorly dispersed by PMMA alone as evidenced by rapid settling and high viscosity. The calculated monolayer adsorption is near that of experimental adsorption.

The experimental adsorption of silane onto TiH$_2$ particles in acetone can be found in Figure 2. Particles not treated with silane (silane dissolved in acetone followed by raw powder addition) showed an experimental adsorption near the predicted value. Silane treated TiH$_2$ showed an adsorption significantly higher than the predicted value, indicating chemical and/or multilayer adsorption.

For TiH$_2$ powder mixed into a solution of acetone and silane, little adsorption occurred and the slurry was paste-like. By treating the powder with a silane/methanol solution, allowing the methanol to evaporate, and subsequently mixing the silane treated powder with acetone, adsorption was greatly improved. Product literature provided by Dow Corning suggests that this is a chemical process, explaining the high degree of adsorption. A possible route to the chemical adsorption of silane onto TiH$_2$ is shown in Figure 3.
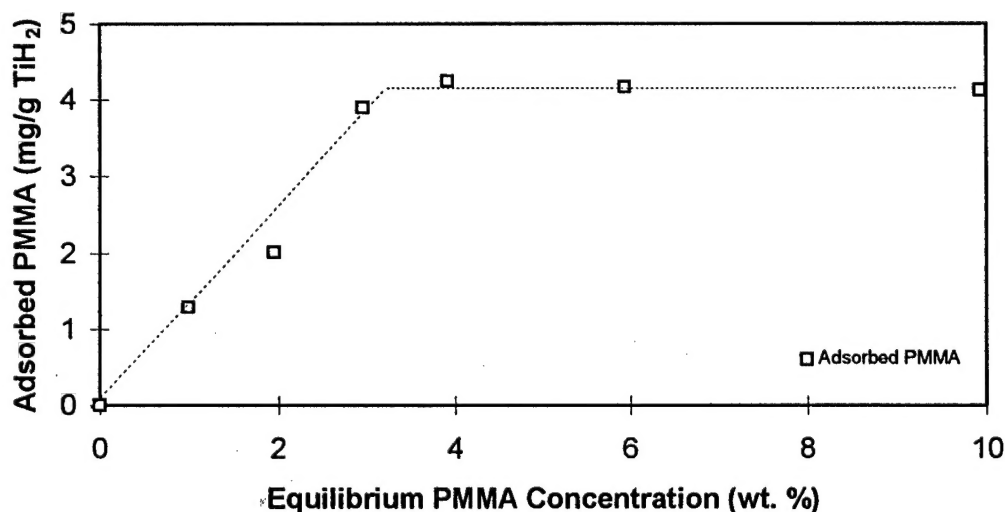

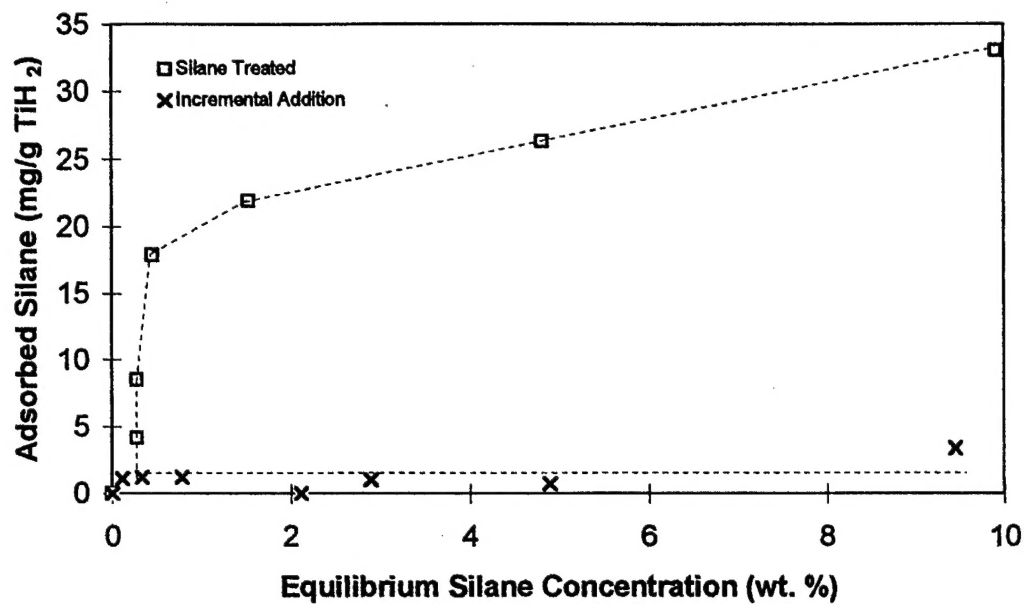Figure 1 Adsorption isotherm for PMMA on TiH$_2$ powder in acetone.

Figure 2 Adsorption isotherm for silane on TiH_2 powder in acetone.
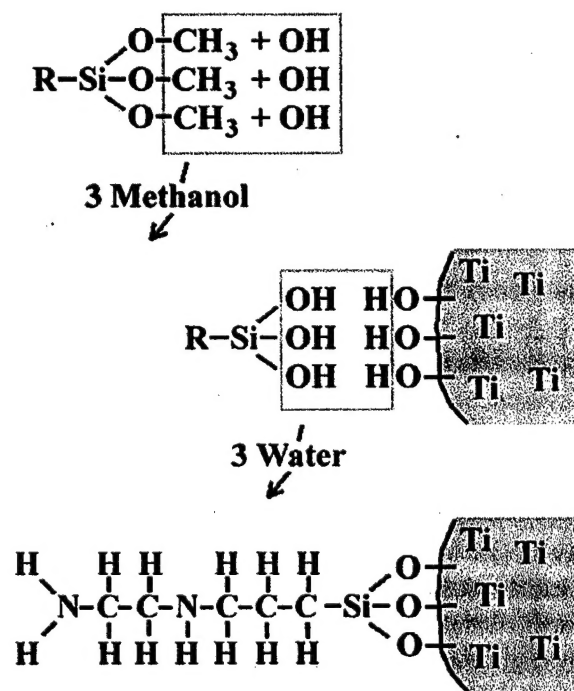

Figure 3 Suggested route to the chemical adsorption of silane onto TiH_2.

The viscosity data presented in Figure 4 is indicative of the degree of dispersion provided by several polymer systems. PMMA alone does not yield low enough viscosity at high solids loading to efficiently process. As a polyester/polyamine copolymer, the dispersant head group of the PS3 polymer molecule exhibits amine functionality. The nitrogen atoms associated with amine groups have unpaired electrons and act as electron donors. This provides a driving force for adsorption and efficiently stabilizes the slurry. Unfortunately, poor evaporation behavior associated with PS3 renders the dispersant unusable. By treating the surface of the TiH_2 powder with silane, low viscosities can be achieved at high solid contents. This is due to the formation of chemical bonds between silane molecules and the hydride particle. The amine groups carry a positive charge and serve as adsorption sites for PMMA. PMMA is then able to sterically disperse the slurry as it does with positively charged oxide powders.

□ 3.5 wt.% 2008 PMMA

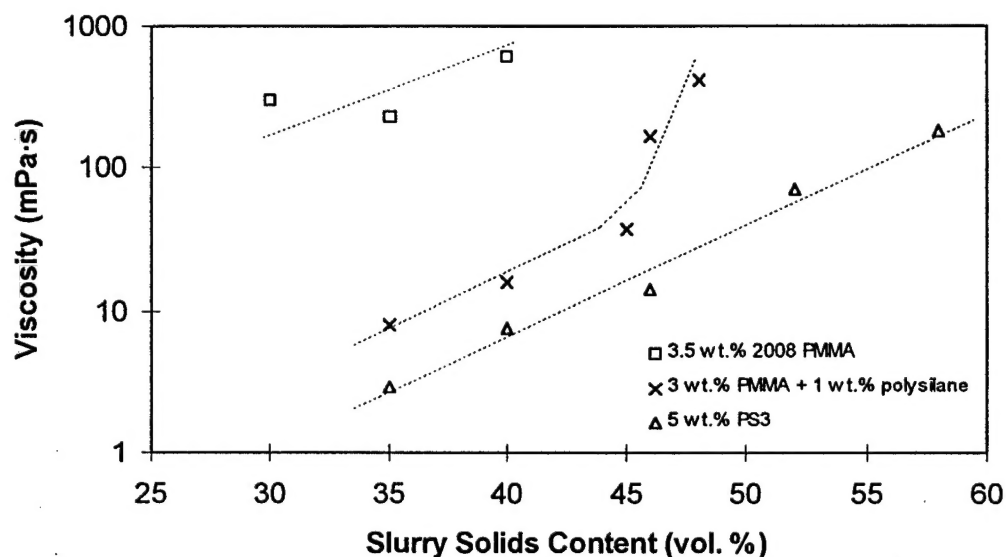× 3 wt.% PMMA + 1 wt.% polysilane

△ 5 wt.% PS3

Figure 4 Effect of solids loading on viscosity for several different dispersant combinations.

CONCLUSIONS

This investigation provides a method of dispersing negatively charged titanium hydride (TiH_2) powder with an anionic surfactant and a particle bonded silane coupling agent. By using the coupling agent, the surface charge of TiH_2 powder can be reversed from negative to positive and PMMA can be employed as a dispersant. By characterizing viscosity, zeta potential, and adsorption behavior, it is possible to optimize slurry preparation techniques and quantify the amount of dispersants required.

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